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(19) (CA) **CANADIAN PATENT** (12)

(54) Process for the Preparation of Hydrocarbons and/or
Oxygen-Containing Hydrocarbon Derivatives and for
Crude Oil Production

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A B S T R A C T

PROCESS FOR THE PREPARATION OF HYDROCARBONS AND/OR
OXYGEN-CONTAINING HYDROCARBON DERIVATIVES
AND FOR CRUDE OIL PRODUCTION

Process for the preparation of hydrocarbons and/or oxygen-containing hydrocarbon derivatives and for the production of crude oil from an underground formation, wherein

- a) a mixture of CO and H₂ is partly converted to hydrocarbons and/or oxygen-containing hydrocarbon derivatives, carbon dioxide being formed;
- b) the hydrocarbons and/or oxygen-containing hydrocarbon derivatives are separated at least partly from the product of step a) and a carbon dioxide-containing off-gas is obtained;
- c) the off-gas is subjected to an oxidation; and
- d) subsequently at least the carbon dioxide of the off-gas is injected at elevated pressure into the underground formation and crude oil is produced from the formation. The presence of methane in gas which is injected into the underground formation is avoided.

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PROCESS FOR THE PREPARATION OF HYDROCARBONS AND/OR
OXYGEN-CONTAINING HYDROCARBON DERIVATIVES
AND FOR CRUDE OIL PRODUCTION

The invention relates to a process for the preparation of hydrocarbons and/or oxygen-containing hydrocarbon derivatives and for the production of crude oil from an underground formation, wherein

- 5 a) a mixture of carbon monoxide and hydrogen at elevated temperature and pressure is partly converted to hydrocarbons and/or oxygen-containing hydrocarbon derivatives, carbon dioxide being formed;
 - b) the hydrocarbons and/or oxygen-containing hydrocarbon
10 derivatives are separated at least partly from the product of step a) and a carbon dioxide-containing off-gas is obtained;
 - c) at least the carbon dioxide of the off-gas is injected at elevated pressure into the underground formation and crude oil is produced from the formation.
- 15 Such a process is known from US patent specification No. 4,098,339. This specification discloses a process in which natural gas with a substantial carbon dioxide content is converted by steam into a mixture of carbon monoxide, hydrogen and carbon dioxide. The carbon dioxide content is raised by means of the water gas shift
20 reaction in which carbon monoxide and steam react to form carbon dioxide and hydrogen. Carbon monoxide and hydrogen in the product are subsequently converted into methanol or liquid hydrocarbons. The methanol or liquid hydrocarbons are separated from the product and an off-gas with a substantial carbon dioxide content is obtained.
- 25 In addition to carbon dioxide, the off-gas still contains some carbon monoxide. This carbon monoxide is converted in a methanator into methane, and the mixture of carbon dioxide and methane is pumped into an oil-bearing underground formation in order to promote the production of crude oil.



It is known that carbon dioxide under pressure dissolves readily in crude oil. This lowers the oil's viscosity and increases the volume of the oil/carbon dioxide mixture so that the now less viscous oil flows more easily out of the pores of the formation.

5 This effect is intensified by the surface tension reduction which is caused by the presence of carbon dioxide and which reduces the cohesion between the oil and the formation.

Oil production techniques using carbon dioxide are known in the art. For example, carbon dioxide injection can be realized via
10 an injection well, part of the carbon dioxide dissolving in the oil while another part, functioning as displacing medium, drives the oil to a production well. Other examples of a displacing medium are water and nitrogen. It is also possible to lower the pressure in the well after the carbon dioxide injection so that the now less
15 viscous oil can be produced through the same well.

It will be clear from the above that the solubility of carbon dioxide in oil is very important. According to the above-mentioned US patent specification, however, the solubility of carbon dioxide in oil is decreased by the presence of methane. The viscosity
20 reduction of the crude oil is therefore not ideal in the known process. In the process according to the present invention the presence of methane is avoided.

The invention therefore relates to a process for the preparation of hydrocarbons and/or oxygen-containing hydrocarbon derivatives and for the production of crude oil from an underground
25 formation, the process comprising the above-mentioned steps a) to c), characterized in that the off-gas is subjected to oxidation to increase the carbon dioxide content before at least the carbon dioxide of the off-gas is injected into the formation.

30 The mixture of carbon monoxide and hydrogen can be obtained in many ways, for example as described in the above-mentioned US patent specification, with the aid of steam reforming of methane. The mixture is, however, preferably obtained from the gasification of a carbon-containing fuel with the aid of an oxygen-containing
35 gas and/or steam. Suitable fuels include many liquid hydrocarbon

fractions, as well as tar, oil from tar sands, shale oil, etc. Solid fuels, such as coal, lignite, peat, etc., can also be employed. Possibilities for the oxygen-containing gas include air, oxygen-enriched air, or almost pure oxygen. The pure oxygen
5 required is usually prepared in an air separation plant. Gasification is generally carried out at a pressure of 5-100 bar and at a temperature of 900-1900 °C.

Depending on the sulphur content of the fuel employed, it is sometimes desirable to subject the gasification product to desulphurization. This is to prevent poisoning of the catalyst in the
10 synthesis step. In addition, a carbon dioxide-rich gas is obtained which contains no hydrogen sulphide. This is desirable, since the transport of H₂S-containing gases by pipeline to the oil field is subject to stringent safety requirements, or even prohibited.

15 The molar ratio of carbon monoxide to hydrogen in the mixture depends on the gasification process employed. In general, the H₂ : CO ratio is between 0.25 and 2. If it is desirable to raise the hydrogen content in the mixture in order to obtain good conversion of the mixture to hydrocarbons and/or oxygen-containing
20 hydrocarbon derivatives, the mixture can be subjected to a water gas shift reaction in which carbon monoxide and steam react to form carbon dioxide and hydrogen.

In the synthesis step the mixture of carbon monoxide and hydrogen is converted to hydrocarbons and/or oxygen-containing
25 hydrocarbon derivatives. Methanol is the most important exponent of the latter group. A suitable catalyst will be necessary if it is intended to synthesize methanol. The most preferred catalysts contain either copper and zinc, or zinc oxide and chromium oxide. Customary pressures and temperatures for methanol synthesis are in
30 the range of 50 to 300 bar and 230 to 350 °C, respectively. Preferably, however, hydrocarbons are prepared. Since hydrocarbons contain no oxygen, in contrast to methanol, an oxygen-containing byproduct is obtained from the synthesis which contains the oxygen originally present in the carbon monoxide. This is water or carbon
35 dioxide, depending on the catalyst chosen. Preferably, catalysts

are chosen which form hydrocarbons and carbon dioxide as almost the only oxygen-containing products, such as the catalysts mentioned below. Aromatic or paraffinic hydrocarbons can be prepared, depending on the catalyst used.

5 If it is wished to prepare aromatic hydrocarbons, it is advantageous to use particular crystalline metal silicates. Particularly advantageous for the preparation of aromatic hydrocarbons together with carbon dioxide is the use of special iron silicates or iron aluminium silicates which are described in
10 British patent specification No 1,555,928 in combination with a catalyst for the synthesis of methanol or dimethyl ether. It is advantageous to employ a mixture of such a silicate and a catalyst for methanol synthesis, such as a $\text{ZnO/Cr}_2\text{O}_3$ composition, as is disclosed in British patent specification No. 2,009,778. The
15 reaction conditions under which the conversion is carried out are usually a pressure of 5 to 100 bar and a temperature of 200 to 500 °C and a space velocity of 300 to 3000 Nl gas/l catalyst/hour.

 If it is wished to prepare predominantly paraffinic hydrocarbons, Fischer-Tropsch catalysts are often used. Particularly
20 suitable catalysts for the preparation of paraffinic hydrocarbons together with carbon dioxide are the iron/magnesium/alumina catalysts described in British patent specification No. 2,053,713, and the iron/chromium/silicate catalysts described in British patent specification No. 2,053,016. The conversion is usually conducted at
25 a temperature of 200 to 450 °C, a pressure of 10 to 70 bar and a space velocity of 500 to 5000 Nl gas/l catalyst/hour.

 The conversion is preferably performed such that more than 90% of the hydrogen present is converted in a single step. In this way a considerable quantity of hydrocarbon products are obtained from
30 the available mixture of carbon monoxide and hydrogen. Moreover, after the separation of the hydrocarbons, the off-gas has a fairly high carbon dioxide content. The carbon dioxide content is then usually above 70 vol.%.

 The desired hydrocarbons and/or oxygen-containing hydrocarbon
35 derivatives are separated in a separating plant. The hydrocarbons

in question will often be the liquid ones; these are hydrocarbons with 5 or more carbon atoms per molecule (C_5^+). Any C_3 and C_4 hydrocarbons formed can also be separated. They can be used as, for example, LPG. Methane and the C_2 hydrocarbons are usually discharged in the off-gas. In addition to CO_2 , H_2O and quantities of unconverted hydrogen and carbon monoxide, the off-gas can therefore also contain combustible constituents, such as methane and C_2 hydrocarbons. In the process according to the invention these combustible hydrocarbons, together with the unconverted quantities of carbon monoxide and hydrogen, are oxidized to form carbon dioxide and water vapour.

The oxidation can be performed with or without a catalyst. If there are only small amounts of combustible constituents present in the off-gas, the oxidation is preferably performed with the aid of a catalyst. A variety of after-burning catalysts are suitable. Preferred catalysts are copper oxide, whether or not on a vanadium pentoxide carrier, or platinum on a carrier such as asbestos. The oxidation is preferably performed at a pressure of 10 to 100 bar and at a temperature in the range of 300 to 1000 °C. After the oxidation, the temperature of the gas can be lowered in a known way to any desired level, recovering usable heat at the same time.

Part of the oxidation products, e.g. water vapour, can be separated from the rest after the oxidation. This can be simply done by cooling until condensation takes place. The rest of the oxidation products, consisting mainly of carbon dioxide, is then injected into the underground formation.

Preferably, however, the entire oxidation product of the off-gas is injected into the formation. The presence of water can be advantageous. The carbon dioxide dissolves in the water that is also injected into the formation. This solution has a weakly acidic effect and can thereby promote the opening of oil-containing pores in the formation. This eases the flow of the oil, rendered less viscous by the carbon dioxide dissolved in it, and thereby also its production. Moreover, the oxidation products do not need to be cooled until the water vapour condenses. The gas can therefore be

injected into the formation at a high temperature, which helps in reducing the viscosity of the crude oil in the formation and thereby eases its production.

The entire oxidation product, or at least the carbon dioxide
5 of the off-gas, is injected into the formation preferably at a pressure of 50 to 400 bar and at a temperature of 20 to 500 °C. In the process according to the invention, carbon dioxide is therefore obtained that has a favourable temperature and has already been brought to an attractively high pressure, which, if desired, can be
10 raised further by compression. The optimum conditions are determined in accordance with the nature of the formation and of the crude oil. The location of the field where the crude oil is produced determines the distance over which the carbon dioxide-containing gas has to be transported. This is a contributory factor in deter-
15 mining the temperature and pressure at which the gas is transported to the field.

In addition to water vapour, the oxidation product of the off-gas can also contain some nitrogen. This occurs if air is used for the oxidation. The solubility of nitrogen in crude oil is,
20 however, much less than that of carbon dioxide. Nitrogen therefore only lowers the viscosity of the oil to a small extent. It can, however, be used as a displacing gas. Preferably, the presence of nitrogen is avoided and the off-gas is oxidized with almost pure oxygen. If the concentration of combustible materials in the
25 off-gas is low, it is highly desirable to use pure oxygen for the oxidation, since oxidation with air proceeds far less readily, and in the absence of a catalyst sometimes does not proceed at all. The oxygen preferably originates from the air separating plant which also supplies the oxygen for the gasification of a carbon-containing
30 fuel with the formation of a mixture of carbon monoxide and hydrogen, said mixture being partially converted into hydrocarbons and/or oxygen-containing hydrocarbon derivatives in step a) of the process.

The oxidation is preferably carried out with a stoichiometric quantity of oxygen. It is, however, not disadvantageous to use a
35 small excess of oxygen. The oxygen is then injected with the carbon

dioxide into the formation. A combustion reaction can there take place between oxygen and oil in which heat is released. This heat lowers the viscosity of the oil.

5 The gas injected into the formation can therefore contain relatively small amounts of water vapour, nitrogen and oxygen. Preferably, however, it contains no more than 10 vol.% impurities, so that a carbon dioxide-rich gas with at least 90 vol.% carbon dioxide is injected into the formation. The gas contains no harmful impurities, such as methane or hydrogen sulphide.

10 From an economical point of view, it is desirable to separate the carbon dioxide from the produced oil and to re-use it. The carbon dioxide recovered from the oil already produced is preferably brought to an elevated pressure and added to the off-gas. This addition to the off-gas can be done either before or after the
15 oxidation. It is advantageous to add the carbon dioxide from the oil after the oxidation, since in this case the oxidation does not need to be carried out with an off-gas having an extra high carbon dioxide content.

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C L A I M S

1. Process for the preparation of hydrocarbons and/or oxygen-containing hydrocarbon derivatives and for the production of crude oil from an underground formation, wherein
 - 5 a) a mixture of carbon monoxide and hydrogen at elevated temperature and pressure is partly converted to hydrocarbons and/or oxygen-containing hydrocarbon derivatives, carbon dioxide being formed;
 - b) the hydrocarbons and/or oxygen-containing hydrocarbon derivatives are separated at least partly from the product of
10 step a) and a carbon dioxide-containing off-gas is obtained;
 - c) at least the carbon dioxide of the off-gas is injected at elevated pressure into the underground formation and crude oil is produced from the formation,
15 characterized in that the off-gas is subjected to an oxidation in order to raise its carbon dioxide content, before at least the carbon dioxide of the off-gas is injected into the formation.
2. Process as claimed in claim 1, characterized in that the entire oxidation product of the off-gas is injected into the formation.
- 20 3. Process as claimed in claim 1 or 2, characterized in that the oxidation of the off-gas is carried out at a pressure of 10 to 100 bar and at a temperature in the range of 300 to 1000 °C.
4. Process as claimed in claim 1 or 2, characterized in that the oxidation is carried out in the presence of a catalyst.
- 25 5. Process as claimed in claim 1 or 2, characterized in that at least the carbon dioxide of the entire oxidation product of the off-gas is injected into the formation at a temperature of 20 to 500 °C and at a pressure of 50 to 400 bar.
6. Process as claimed in claim 1, characterized in that the
30 off-gas is oxidized with almost pure oxygen.

7. Process as claimed in claim 6, characterized in that the oxygen is obtained from an air separating plant which also supplies the oxygen for the gasification of a carbon-containing fuel with the formation of a mixture of carbon monoxide and hydrogen, said mixture being partially converted in step a).
- 5 8. Process as claimed in claim 1 or 2, characterized in that the oxidation is carried out with a stoichiometric quantity of oxygen.
9. Process as claimed in claim 1 or 2, characterized in that the gas injected into the formation contains at least 90 vol.% carbon dioxide.
- 10 10. Process as claimed in claim 1 or 2, characterized in that carbon dioxide recovered from oil already produced is added to the off-gas.



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